The Uses of Isothermal Plastometry

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The most widely used characterization of coal fluidity is the plastometric method developed by Gieseler (1). In a modified form, with a torque clutch replacing the original pulleys and weights, this has become a standard American procedure (2). Its relationship to dilatometry is well established (3-6).

The standard 3 deg/min Gieseler analysis provides a fixed-angle 'slice' across the fluidity-temperature surface, and in a single determination may provide plasticity information across a span of 50-100 deg C. It often reveals fluidity differences of more than a thousandfold among coals of similar rank and chemical composition.

There are, however, several advantages to be gained by conducting Gieseler analyses under isothermal conditions. The resulting data permit the estimation of 'melting' and 'coking' rates and hence (from several runs at different temperatures) the determination of temperature dependencies of these rates. Isothermal data generally provide better simulation of the fluidity characteristics of coal in an actual continuous process such as extrusion feeding (7-9). Isothermal data clearly distinguish among coals of differing temperatures of maximum fluidity.

Fitzgerald has shown that when ln(fluidity) is plotted against time under isothermal conditions the coking slope is substantially linear. The coking slopes of a group of English coals in his study exhibit Arrhenius temperature dependencies, with activation energies in the vicinity of 50 kcal (10,11).

We have confirmed these observations for a group of 29 hvb coals from the eastern mid-continent beds. For most of these coals the isothermal melting curve is also found to be substantially linear (12,13). Figure 1 illustrates a typical isothermal run. The data provide not only classical information (softening point, time of maximum fluidity, solidification point and maximum observed fluidity) but also estimates of the melting and coking slopes and an additional measure, intersection maximum fluidity. This last is obtained by extrapolation of the two slopes to their point of intersection.

Intersection maximum fluidity has several advantages over observed maximum fluidity. Some coals have a flattish and poorly defined region of maximum fluidity. Coals which outgas vigorously are likely to produce irregular and irreproducible readings in the vicinity of maximum fluidity. Highly plastic coals may develop fluidity in excess of 30,000 ddpm, greater than can be measured by the Gieseler plastometer. In all such cases the intersection maximum fluidity is accessible and in our experience is a more consistent and reproducible measure, even for the case of ASTM temperature-gradient runs (Figure 2).

In the present study a number of freshly sampled coals from active mines and coal cleaning plants have been obtained and reduced, stored under inert gas at -40^{o}, and then analyzed using a research model Gieseler plastometer (Standard Instrumentation), sensitive to 0.1 ddpm (roughly 100 megapoise for a Newtonian fluid). Three of these coals are characterized in Table 1.

When a coal is examined in a series of isothermal runs, both melting and coking slopes are steeper at higher temperatures. These trends are illustrated in Figure 3. For this moderately plastic coal, maximum fluidity is increased over tenfold by raising temperature from 412 to 431°C.

Figure 4 is an Arrhenius plot based upon 20 isothermal runs at 412-438°C with Coal #41. The top slope shows the variation of ln ln(intersection maximum fluidity) with reciprocal temperature. The middle and lower slopes show the corresponding variations of ln(melting slope) and ln(coking slope). Each of these is essentially linear over the experimental range.

During an isothermal Gieseler run the solder-pot furnace maintains a nearly constant temperature (standard deviation less than 1.0°C). The linearity of the Arrhenius slopes permits the determination of activation energies with fairly good precision (Table 2). The Arrhenius relationship also permits the interpolation of data so that slopes and fluidities of a number of coals can be determined at precisely the same temperature.

Overall isothermal fluidity characteristics of these and other coals which we are studying (14) are summarized in Table 3. These data suggest some general trends among hvb coals. Activation energies of the coking slopes are all in the vicinity of 50 kcal, as Fitzgerald found with English coals (11). Coking slope values are slightly higher for the sparingly plastic coals. Activation energies of the melting slopes tend to increase with increasing plasticity, from 25-30 kcal for sparingly plastic coals to 50-55 kcal for highly plastic coals. Activation energies of ln(maximum fluidity) decrease with increasing plasticity, from 30-35 kcal for sparingly plastic coals to 10-20 kcal for highly plastic coals. The ratio (melting slope) / (coking slope) is notably higher for the highly plastic coals.

Maximum fluidities measured under isothermal conditions, at or near the ASTM temperature of maximum fluidity, are substantially greater than the corresponding ASTM maximum fluidities. For sparingly fluid coals the maximum isothermal fluidity is typically two- to three-fold that observed in an ASTM run. This ratio increases with coal fluidity, with values typically in the range 5-8 for moderately plastic (30-300 ddpm) coals. Table 4 summarizes this trend for 17 coals for which isothermal data have been obtained at or very near the ASTM temperature of maximum fluidity. For highly fluid coals the isothermal data was obtained at temperatures appreciably below T(max flu). The maximum fluidity obtained in an ASTM run can be matched in an isothermal run conducted at 10-15 deg C below the ASTM temperature of maximum fluidity.

Discussion.

Since a very large number of parallel reactions is involved in both the melting and coking regions of an isothermal run, it is reasonable to ask why - for a semilogarithmic plot or any other plot - the change in fluidity with time has domains of substantial linearity. The condition necessary to find linearity under some conditions is that the major contributing reactions be of the same kinetic order:

$$-d[B]/dt = w_1k_1[B]^n + w_2k_2[B]^n + \ldots \qquad (1)$$

where the w_i's and k_i's denote weighting factors and empirical rate constants.

The right-hand terms are then easily collected into a single term. The observation that plots of ln(fluidity) vs. time yield melting and coking slopes which are essentially linear suggests that Equation 1 is in fact followed.

This does not mean, as some have suggested, that isothermal coking is a set of first-order processes. Since slurry fluidity is not a linear function of fluid fraction, the coking process is not kinetically first-order. Further work is needed before kinetic dependencies can be inferred from these curves.

Since melting and coking slopes and ln(maximum fludity) all follow Arrhenius dependencies, the fluidity span (the time interval during which fluidity exceeds a specified value) can also be calculated at any interpolated temperature. This can be seen analytically. If f is ln(intersection maximum fluidity), tm the time interval from initial softening to maximum fluidity and tc the time interval from maximum fluidity to coking point, then the melting slope m is equal to f/tm and the coking slope c is equal to f/tc. The total time span (tm + tc) is then:

$$t = f*(1/m + 1/c) \qquad (2)$$

If a process requires a minimum fluidity F' which is any value less than the maximum fludity, then:

$$t' = (f - f') * (1/m + 1/c) \qquad (3)$$

where $f' = \ln(F')$.

This study is part of an investigation into the predictability of plastic behavior in bituminous coals (14). We acknowledge with thanks the support of this work by the U.S. Department of Energy.

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Table 1
Coal Characterization Data*

	Coal #18	Coal #22	Coal #41
County	Muhlenberg	Union	Butler
Seam and rank	KY #9, hvBb	KY #6, hvAb	Amos, hvBb
Moisture	7.09%	2.40%	7.78%
Ash	8.36	9.60	2.77
Volatile matter	40.6	39.4	42.1
% Carbon	74.1	76.0	80.7
% Hydrogen	5.11	5.42	5.74
% Nitrogen	1.50	1.44	1.61
% Sulfur	3.59	2.91	1.06
Heating value, Btu/lb	13,020	13,490	14,280
Free swelling index	4.5	8.	3.
% Vitrinite	76.1%	70.7%	79.0%
% Pseudovitrinite	1.2	5.3	6.7
% Exinite	3.5	3.2	6.3
% Resinite	0.4	0.5	0.9
% Fusinite	3.3	3.5	0.4
% Semifusinite	3.6	2.8	0.7
% Micrinite	1.7	1.9	2.7
% Macrinite	0.2	0.1	0.0
Mineral matter (Parr)	11.0	12.0	3.3
Vitrinite max reflect	0.54	0.73	0.67
ASTM Gieseler data:			
T(softening)**	388	376	398
T(max fluidity)	428	422-435	436
T(solidification)**	447	467	459
Max fluidity (observed)	26.8	>30,000	217
Max fluidity (intersctn)	44.5	2.61E+6	590

* Moisture is as determined, other values on a dry ash-included basis.
** Temperature at which fluidity value is 1.0 ddpm.

Table 2
Precision of Arrhenius Temperature Dependencies*

Coal	n	Melting slope	Coking slope	ln(Intersection max flu)
#18	20	31.0 ± 2.5	48.5 ± 3.2	35.9 ± 2.5
#22	19	56.5 ± 1.8	48.7 ± 2.0	20.0 ± 1.5
#41	20	43.8 ± 1.8	51.4 ± 2.0	19.7 ± 0.8

* Least-squares values in kcal and standard deviations.

Table 3

Fluidity Characteristics of Selected Coals*

Coals	Intersection max flu			Melting slope[1]			Coking slope[1]		
	400°C	420°C	E(a)	400°C	420°C	E(a)	400°C	420°C	E(a)
#22	2540	1.8E5	20.0	0.70	2.38	56.5	0.13	0.37	48.7
average of 5 other highly plastic coals	14300	2.5E5	12.3	0.99	3.0	51.	0.16	0.43	44.5
#41	40	277	19.7	0.24	0.62	43.8	0.14	0.43	51.4
average of 5 other medium plastic coals	40	366	21.4	0.34	0.82	42.1	0.19	0.53	48.7
#18	8	88	35.9	0.40	0.77	31.0	0.27	0.77	48.5
average of 5 other slightly plastic coals	5	24	33.2	0.35	0.62	26.9	0.20	0.60	50.8

* Fluidity averages are logarithmic. Properties averaged from coals 21, 25, 27, 32 and 34 (highly plastic); 15, 26, 36, 37 and 39 (medium plastic); and 02, 03, 09, 24 and 40 (slightly plastic), ref. 15.

[1] Slopes are in reciprocal minutes.

Table 4

Maximum Observed Fluidities under ASTM and Isothermal Conditions

no. of coals	Maximum fluidity (MF) range, ddpm	ASTM Conditions Avg MF	ASTM Conditions Avg T	Isothermal Conditions Avg MF	Isothermal Conditions Avg T	Ratio*
5	2 < MF < 8	3.8	422°	10.2	421°	2.7
6	8 < MF < 32	12.8	426°	51.2	426°	4.0
6	32 < MF < 256	136.	430°	829.	430°	6.1

* Ratio of (maximum isothermal fluidity) / (maximum ASTM fluidity)

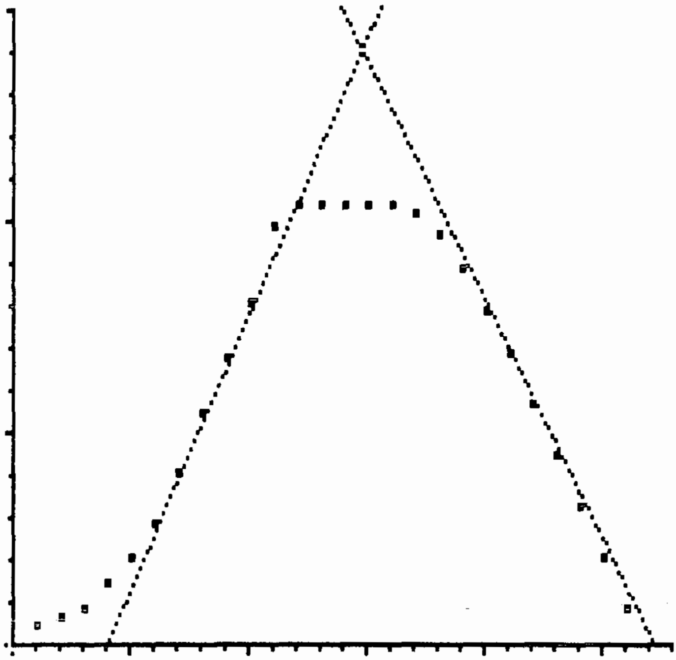

FIGURE 2. ASTM PLASTOMETRY OF A hvAb COAL. Horizontal: time in minutes, scale 0 to 28. Vertical: ln(fluidity in ddpm), scale 0 to 15. The flat top of the experimental curve marks the instrument limit of 30,000 ddpm.

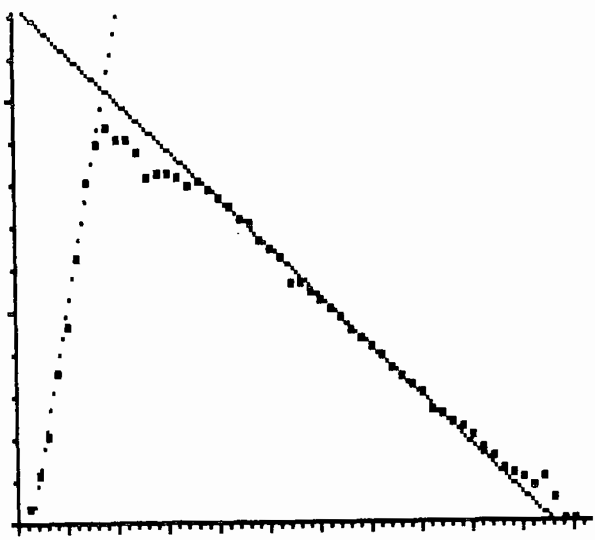

FIGURE 1. ISOTHERMAL PLASTOMETRY OF A hvAb COAL AT 405°C. Horizontal: time in minutes, scale 0 to 56. Vertical: ln(fluidity in ddpm), scale 0 to 12. Slope calculations use fluidities above 10 ddpm and below one quarter of the observed maximum fluidity.

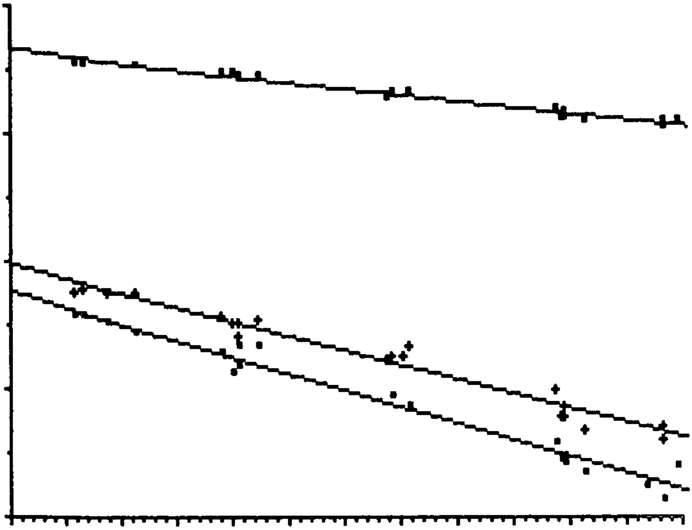

FIGURE 4. ARRHENIUS PLOT OF FLUIDITY CHARACTERISTICS OF COAL #41. Horizontal: 1000/°K, scale 1.40 to 1.46 (441-412°C). Vertical: ln(function), scale -1.5 to +2.5. From top to bottom: ln(maximum fluidity), melting slope, coking slope.

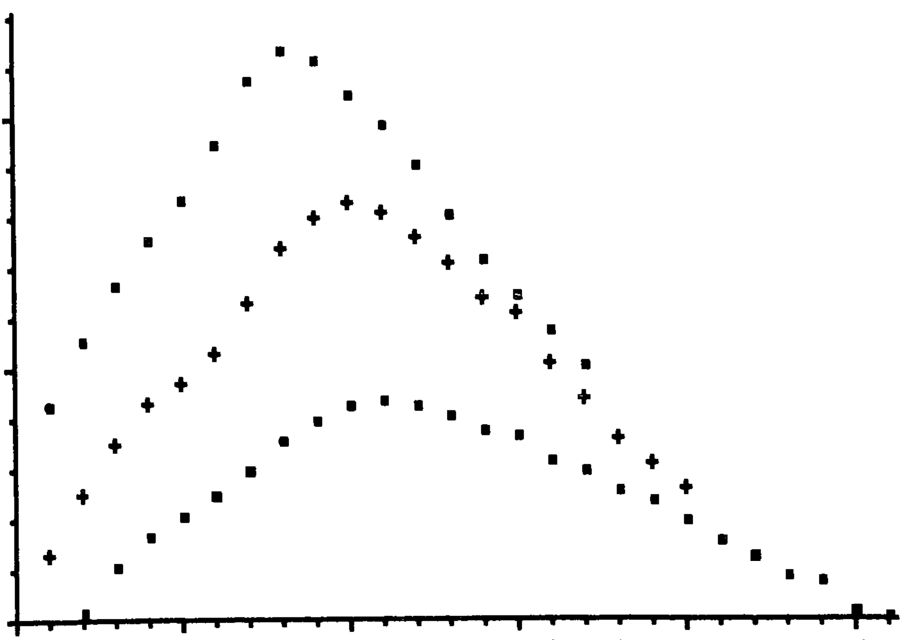

FIGURE 3. ISOTHERMAL PLASTOMETRY OF COAL #41 AT 431, 424 AND 412°C. Horizontal: time in minutes, scale 0 to 26. Vertical: ln(fluidity in ddpm), curves offset.